SUPPORTING INFORMATION

Alkyltin Clusters: The Less Symmetric Keggin Isomers

Danielle C. Hutchison [a], Rebecca D. Stern [b], Morgan R. Olsen [a], Lev N. Zakharov [a], Kristin A. Persson [b,c], May Nyman [a]

[a]Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331 (USA)
[b]Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720 (USA)
[c]Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (USA)

Table of Contents:

Tables and Figures:

Fig. SI7: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)\ (O)_4(OH)_7(OCH_3)_{13}]^{1+}$.

Fig. SI8: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)\ (O)_5(OH)_6(OCH_3)_{12}]^{1+}$.

Fig. SI9: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_5(OH)_{13}(OCH_3)_9(CH_3OH)_9]^{1+}$.

Figure SI10: Size distribution analysis of SAXS data of γ-$NaSn_{12}$ in benzene.

Figure SI11: Modelling II results for β,γ-$NaSn_{12}$ in benzene. The experimental scattering curve is in red and the calculated model in gray. The calculated radius is consistent with the radius determined from the experimental crystal structure.

Figure SI12: FTIR spectrum for β,γ-$NaSn_{12}$

Bond Valence Sum for Oxo Ligands of Clusters

Table SI1: BVS for Oxo Ligands of β-$NaSn_{12}$.

Assignment	Atom 1	Atom 2	d (A)	BV	BVS
O^{2-} Central oxo	O1	Sn1	2.090(16)	0.6	2.09
	O1	Sn2	2.085(10)	0.6	
	O1	Sn2	2.085(10)	0.6	
	O1	Na1	2.314(19)	0.3	
O^{2-} Central oxo	O2	Sn3	2.075(15)	0.6	2.16
	O2	Sn4	2.067(9)	0.6	
	O2	Sn4	2.067(9)	0.6	
	O2	Na1	2.330(16)	0.2	
O^{2-} Central oxo	O3	Sn5	2.094(12)	0.6	2.09
	O3	Sn6	2.075(12)	0.6	
	O3	Sn7	2.082(13)	0.6	
	O3	Na1	2.326(12)	0.2	
OH^-	O5	Sn1	2.033(14)	0.7	1.34
	O5	Sn5	2.074(15)	0.6	
O^{2-}	O7	Sn2	2.031(12)	0.7	1.39
	O7	Sn3	2.051(12)	0.7	
OH^-	O8	Sn2	2.084(14)	0.6	1.24
	O8	Sn6	2.079(14)	0.6	
O^{2-}	O11	Sn4	2.056(13)	0.7	1.38
	O11	Sn6	2.030(12)	0.7	
OH^-/O^{2-}	O12	Sn4	2.067(13)	0.6	1.35

	O12	Sn7	2.033(13)	0.7	
OH^-	O16	Sn5	2.065(7)	0.6	1.30
	O16	Sn5	2.065(7)	0.6	
OH^-	O17	Sn7	2.116(7)	0.6	1.13
	O17	Sn7	2.116(7)	0.6	
OCH_3^-	O4	Sn1	2.145(15)	0.5	1.87
	O4	Sn2	2.161(14)	0.5	
	O4	C29	1.45(3)	0.8	
OCH_3^-	O6	Sn2	2.133(13)	0.5	1.86
	O6	Sn2	2.133(13)	0.5	
	O6	C30	1.48(4)	0.8	
OCH_3^-	O9	Sn4	2.162(12)	0.5	1.77
	O9	Sn4	2.162(12)	0.5	
	O9	C31	1.48(4)	0.8	
OCH_3^-	O10	Sn3	2.119(13)	0.6	2.21
	O10	Sn4	2.178(13)	0.5	
	O10	C32	1.33(3)	1.2	
OCH_3^-	O13	Sn5	2.15116	0.5	1.87
	O13	Sn2	2.15316	0.5	
	O13	C33	1.453	0.8	
OCH_3^-	O14	Sn5	2.132(17)	0.5	2.05
	O14	Sn7	2.147(15)	0.5	
	O14	C34	1.39(3)	1.0	
OCH_3^-	O15	Sn6	2.094(17)	0.6	1.86
	O15	Sn7	2.148(17)	0.5	
	O15	C35	1.50(3)	0.7	

Table SI2: BVS for Oxo Ligands of γ-$NaSn_{12}$.

Assignment	**Atom 1**	**Atom 2**	**d (A)**	**BV**	**BVS**
O^{2-} Central oxo	O1	Sn1	2.114(11)	0.6	2.00
	O1	Sn2	2.102(11)	0.6	
	O1	Sn3	2.091(10)	0.6	
	O1	Na1	2.339(12)	0.2	
O^{2-} Central oxo	O2	Sn4	2.062(11)	0.7	2.07
	O2	Sn5	2.079(9)	0.6	
	O2	Sn6	2.125(10)	0.6	
	O2	Na1	2.329(12)	0.2	
O^{2-} Central oxo	O3	Sn7	2.078(9)	0.6	2.05

	O3	Sn8	2.074(11)	0.6	
	O3	Sn9	2.121(10)	0.6	
	O3	Na1	2.336(12)	0.2	
O^{2-} Central oxo	O4	Sn10	2.082(9)	0.6	2.03
	O4	Sn11	2.081(10)	0.6	
	O4	Sn12	2.118(10)	0.6	
	O4	Na1	2.356(11)	0.2	
O^{2-}	O17	Sn2	2.035(11)	0.7	1.35
	O17	Sn7	2.066(11)	0.6	
OH^-	O18	Sn2	2.072(12)	0.6	1.21
	O18	Sn8	2.1081(1)	0.6	
OH^-	O19	Sn3	2.074(12)	0.6	1.23
	O19	Sn10	2.091(12)	0.6	
OH^-	O20	Sn3	2.110(11)	0.6	1.13
	O20	Sn10	2.123(12)	0.6	
OH^-	O21	Sn1	2.078(12)	0.6	1.22
	O21	Sn4	2.097(11)	0.6	
OH^-	O22	Sn4	2.065(11)	0.6	1.31
	O22	Sn12	2.059(11)	0.7	
O^{2-}	O23	Sn1	2.042(10)	0.7	1.38
	O23	Sn5	2.043(10)	0.7	
OH^-	O24	Sn5	2.100(13)	0.6	1.33
	O24	Sn7	2.017(13)	0.7	
O^{2-}	O25	Sn6	2.040(12)	0.7	1.35
	O25	Sn9	2.064(11)	0.7	
O^{2-}	O26	Sn6	2.037(9)	0.7	1.38
	O26	Sn12	2.045(10)	0.7	
O^{2-}	O27	Sn9	2.039(10)	0.7	1.41
	O27	Sn10	2.031(10)	0.7	
OH^-	O28	Sn8	2.080(11)	0.6	1.22
	O28	Sn11	2.094(11)	0.6	
OCH_3^-	O5	Sn1	2.143(12)	0.5	1.99
	O5	Sn2	2.147(12)	0.5	
	O5	C49	1.41(2)	0.9	
OCH_3^-	O6	Sn1	2.128(11)	0.5	1.95
	O6	Sn3	2.196(12)	0.5	
	O6	C50	1.41(2)	0.9	
OCH_3^-	O7	Sn2	2.138(11)	0.5	1.92
	O7	Sn3	2.149(12)	0.5	
	O7	C51	1.44(2)	0.9	

OCH_3^-	O8	Sn4	2.144(11)	0.5	1.86
	O8	Sn5	2.184(13)	0.5	
	O8	C52	1.44(2)	0.9	
OCH_3^-	O9	Sn4	2.146(11)	0.5	1.88
	O9	Sn6	2.170(13)	0.5	
	O9	C53	1.44(2)	0.9	
OCH_3^-	O10	Sn5	2.173(11)	0.5	1.90
	O10	Sn6	2.144(10)	0.5	
	O10	C54	1.43(2)	0.9	
OCH_3^-	O11	Sn7	2.190(13)	0.5	1.88
	O11	Sn8	2.114(12)	0.6	
	O11	C55	1.45(2)	0.8	
OCH_3^-	O12	Sn7	2.152(11)	0.5	1.87
	O12	Sn9	2.172(11)	0.5	
	O12	C56	1.44(2)	0.9	
OCH_3^-	O13	Sn8	2.150(12)	0.5	1.89
	O13	Sn9	2.159(13)	0.5	
	O13	C57	1.44(2)	0.9	
OCH_3^-	O14	Sn10	2.156(11)	0.5	2.10
	O14	Sn11	2.153(10)	0.5	
	O14	C58	1.36(2)	1.0	
OCH_3^-	O15	Sn10	2.171(12)	0.5	2.05
	O15	Sn12	2.131(10)	0.5	
	O15	C59	1.38(2)	1.0	
OCH_3^-	O16	Sn11	2.149(12)	0.5	2.00
	O16	Sn12	2.192(12)	0.5	
	O16	C60	1.38(2)	1.0	

Table SI3: BVS for Oxo Ligands of γ-$NaSn_{13}$.

Assignment	Atom 1	Atom 2	d (Å)	BV	BVS
O^{2-} Central oxo	O1	Sn1	2.084(13)	0.6	2.00
	O1	Sn2	2.138(16)	0.5	
	O1	Sn3	2.093(17)	0.6	
	O1	Na1	2.324(16)	0.2	
O^{2-} Central oxo	O2	Sn4	2.05(2)	0.7	2.09
	O2	Sn5	2.111(16)	0.6	
	O2	Sn6	2.102(15)	0.6	

	O2	Na1	2.31(2)	0.2	
O^{2-} Central oxo	O3	Sn7	2.110(17)	0.6	2.02
	O3	Sn8	2.106(13)	0.6	
	O3	Sn9	2.086(18)	0.6	
	O3	Na1	2.320(15)	0.2	
O^{2-} Central oxo	O4	Sn10	2.100(16)	0.6	2.15
	O4	Sn11	1.99(3)	0.8	
	O4	Sn12	2.108(16)	0.6	
	O4	Na1	2.40(2)	0.2	
O^{2-}	O17	Sn1	2.102(15)	0.6	2.04
	O17	Sn8	2.143(15)	0.5	
	O17	Sn13	1.931(15)	0.9	
OH^-	O18	Sn1	2.036(15)	0.7	1.30
	O18	Sn8	2.098(16)	0.6	
OH^-	O19	Sn2	2.095(18)	0.6	1.17
	O19	Sn4	2.112(16)	0.6	
O^{2-}	O20	Sn2	2.019(16)	0.7	1.48
	O20	Sn6	2.015(16)	0.7	
O^{2-}	O21	Sn3	2.042(17)	0.7	1.79
	O21	Sn11	2.087(15)	0.6	
	O21	Sn13	2.172(16)	0.5	
O^{2-}	O22	Sn3	2.081(16)	0.6	1.31
	O22	Sn12	2.045(16)	0.7	
OH^-	O23	Sn4	2.105(16)	0.6	1.16
	O23	Sn7	2.111(19)	0.6	
O^{2-}	O24	Sn5	2.024(16)	0.7	1.45
	O24	Sn7	2.024(16)	0.7	
O^{2-}	O25	Sn5	2.18(3)	0.5	1.33
	O25	Sn10	1.96(3)	0.9	
OH^-	O26	Sn6	2.02(3)	0.7	1.30
	O26	Sn12	2.11(3)	0.6	
OH^-	O27	Sn9	2.102(17)	0.6	1.27
	O27	Sn10	2.044(16)	0.7	
O^{2-}	O28	Sn9	2.104(17)	0.6	1.85
	O28	Sn11	2.111(15)	0.6	
	O28	Sn13	2.041(16)	0.7	
OH^-	O12	Sn8	2.148(18)	0.5	1.07
	O12	Sn9	2.124(14)	0.6	
OCH_3^-	O5	Sn1	2.191(16)	0.5	1.84
	O5	Sn3	2.140(14)	0.5	

	O5	C53	1.45(3)	0.8	
OCH_3^-	O6	Sn1	2.113(16)	0.6	2.05
	O6	Sn2	2.148(14)	0.5	
	O6	C54	1.40(3)	1.0	
OCH_3^-	O7	Sn2	2.147(18)	0.5	1.80
	O7	Sn3	2.163(18)	0.5	
	O7	C55	1.48(3)	0.8	
OCH_3^-	O8	Sn4	2.09(2)	0.6	1.95
	O8	Sn5	2.17(3)	0.5	
	O8	C56	1.44(5)	0.9	
OCH_3^-	O9	Sn5	2.178(18)	0.5	1.89
	O9	Sn6	2.149(18)	0.5	
	O9	C57	1.43(3)	0.9	
OCH_3^-	O10	Sn4	2.094(18)	0.6	1.85
	O10	Sn10	2.18(3)	0.5	
	O10	C58	1.48(4)	0.8	
OCH_3^-	O11	Sn8	2.154(14)	0.5	2.11
	O11	Sn9	2.117(17)	0.6	
	O11	C59	1.37(6)	1.0	
OCH_3^-	O13	Sn7	2.131(19)	0.5	1.87
	O13	Sn9	2.190(18)	0.5	
	O13	C61	1.44(3)	0.9	
OCH_3^-	O14	Sn10	2.25(3)	0.4	1.95
	O14	Sn11	2.053(18)	0.7	
	O14	C62	1.43(4)	0.9	
OCH_3^-	O15	Sn10	2.163(18)	0.5	1.84
	O15	Sn12	2.163(18)	0.5	
	O15	C63	1.45(4)	0.8	
OCH_3^-	O16	Sn11	2.090(18)	0.6	1.88
	O16	Sn12	2.21(3)	0.4	
	O16	C64	1.45(5)	0.8	
OCH_3^- On capping tin	O29	Sn13	2.063(18)	0.7	1.73
	O29	C65	1.36(4)	1.1	

Complete ESI-MS Peak Assignments

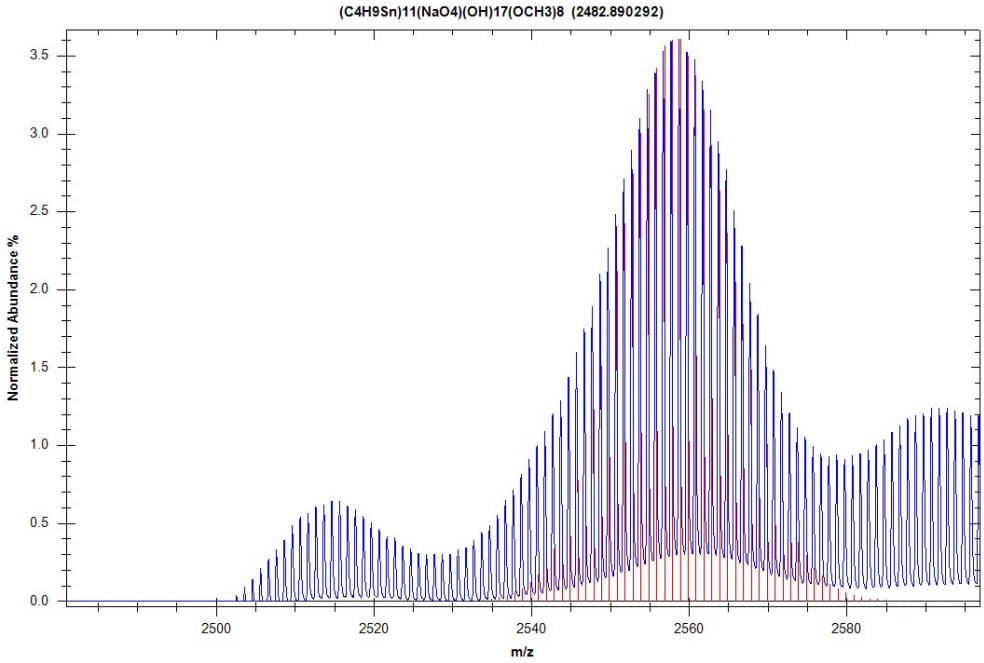

Fig. SI1: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{11}(NaO_4)(OH)_{17}(OCH_3)_{12}]^{1+}$.

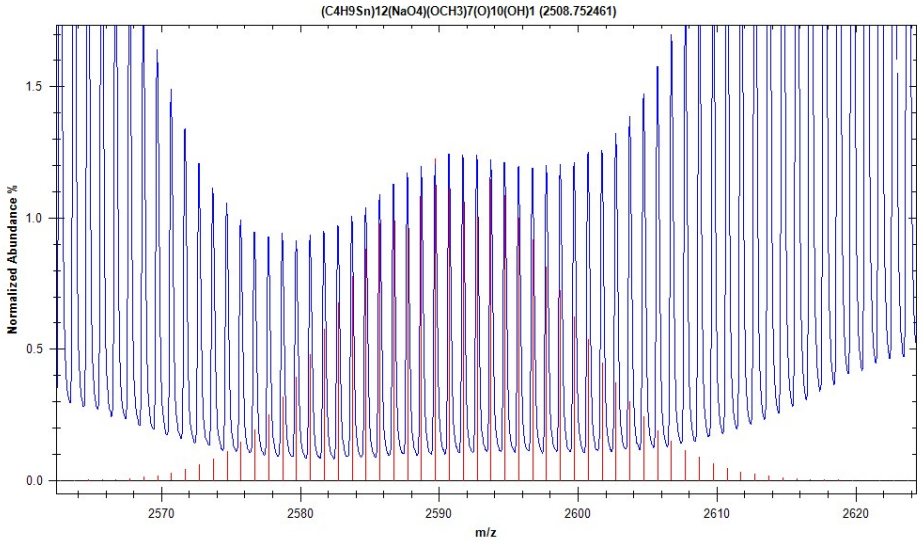

Fig. SI2: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_{10}(OH)(OCH_3)_7]^{1+}$.

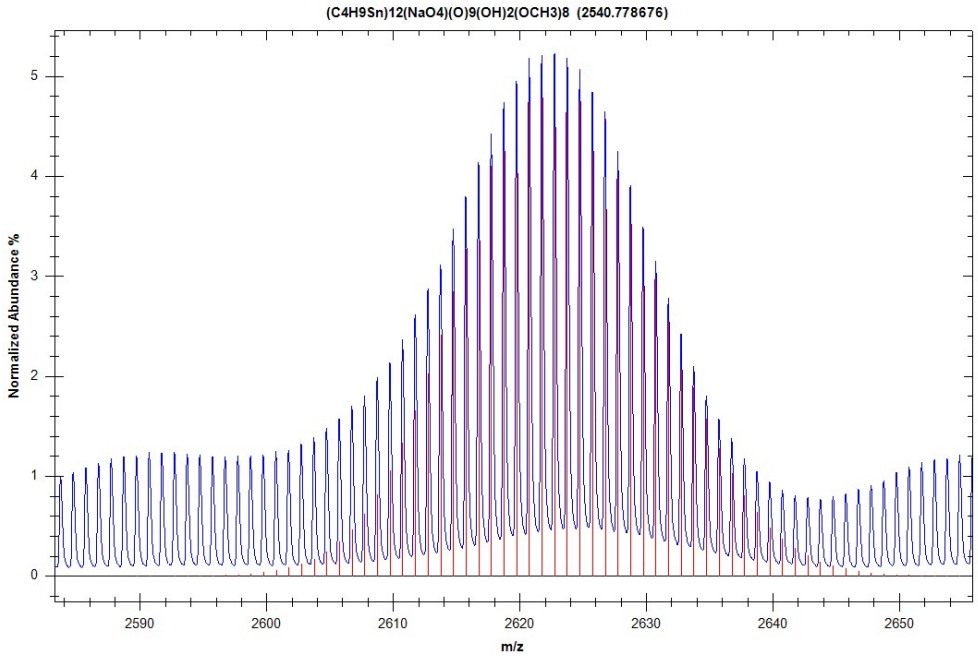

Fig. SI3: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_9(OH)_2(OCH_3)_8]^{1+}$.

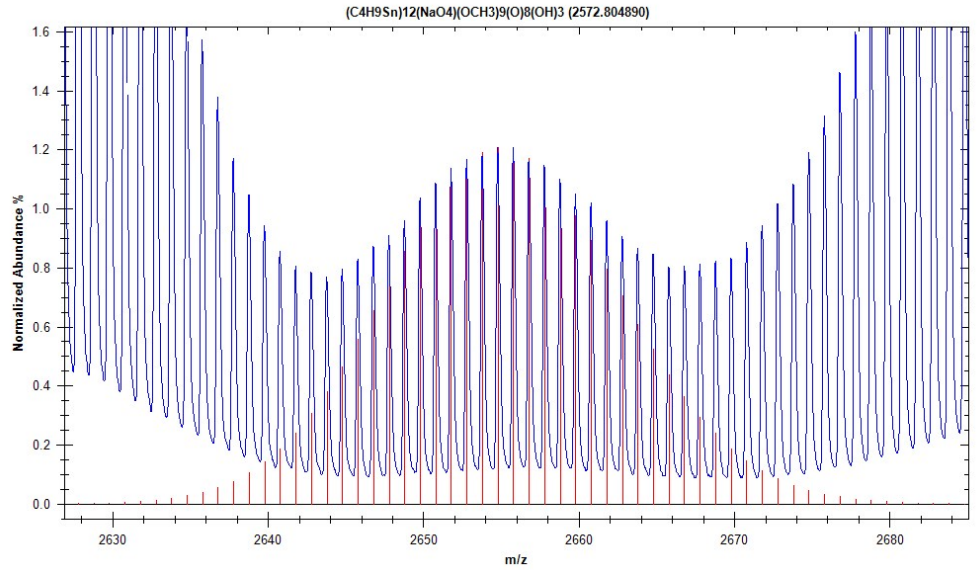

Fig. SI4: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_8(OH)_3(OCH_3)_9]^{1+}$.

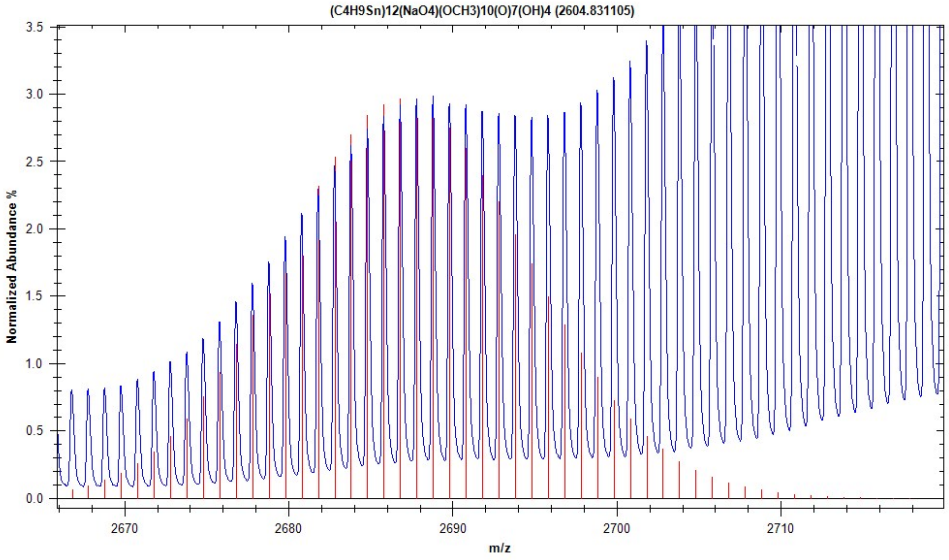

Fig. SI5: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_7(OH)_4(OCH_3)_{10}]^{1+}$.

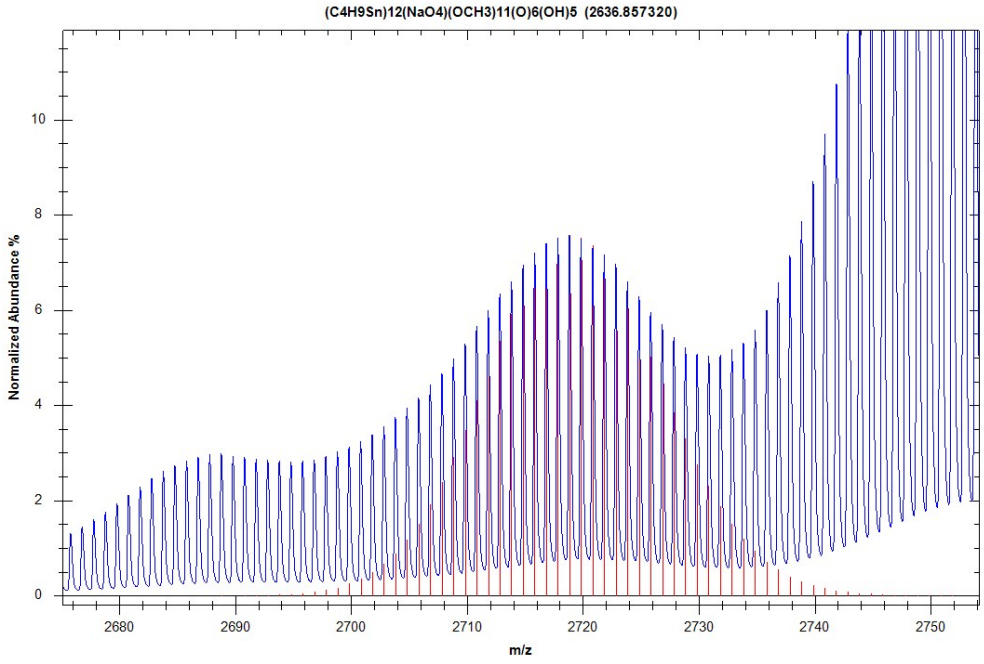

Fig. SI6: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)\ (O)_6(OH)_5(OCH_3)_{11}]^{1+}$.

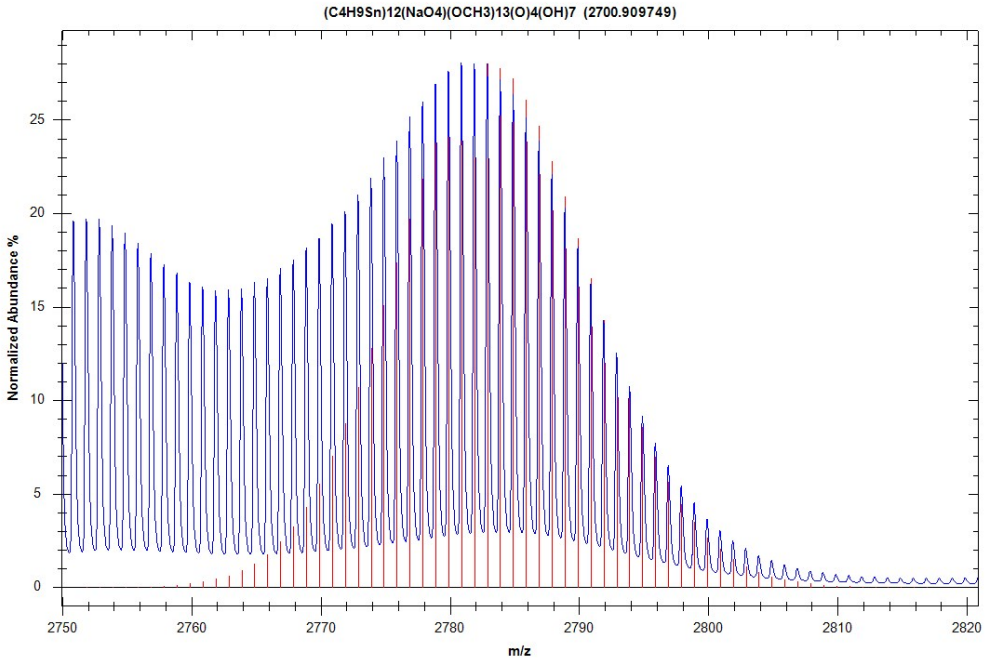

Fig. SI7: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_4(OH)_7(OCH_3)_{13}]^{1+}$.

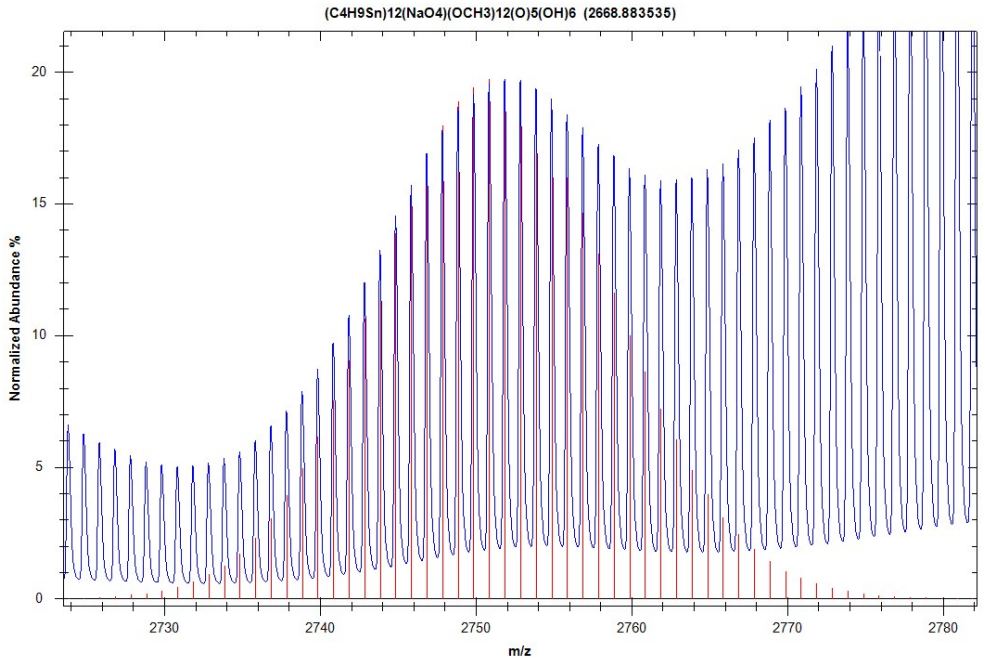

Fig. SI8: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)\ (O)_5(OH)_6(OCH_3)_{12}]^{1+}$.

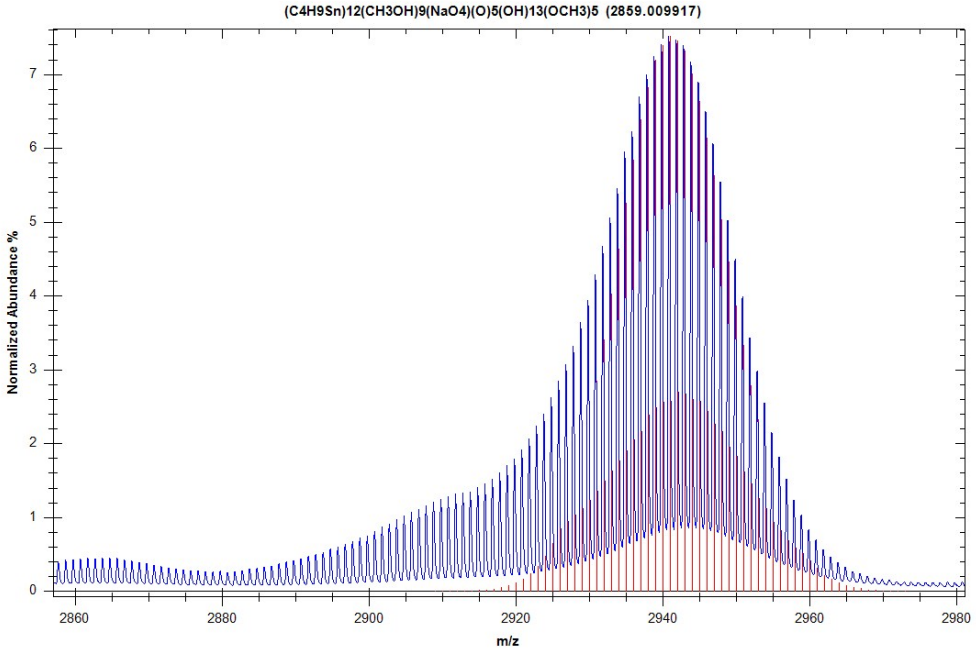

Fig. SI9: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(NaO_4)(O)_5(OH)_{13}(OCH_3)_9(CH_3OH)_9]^{1+}$.

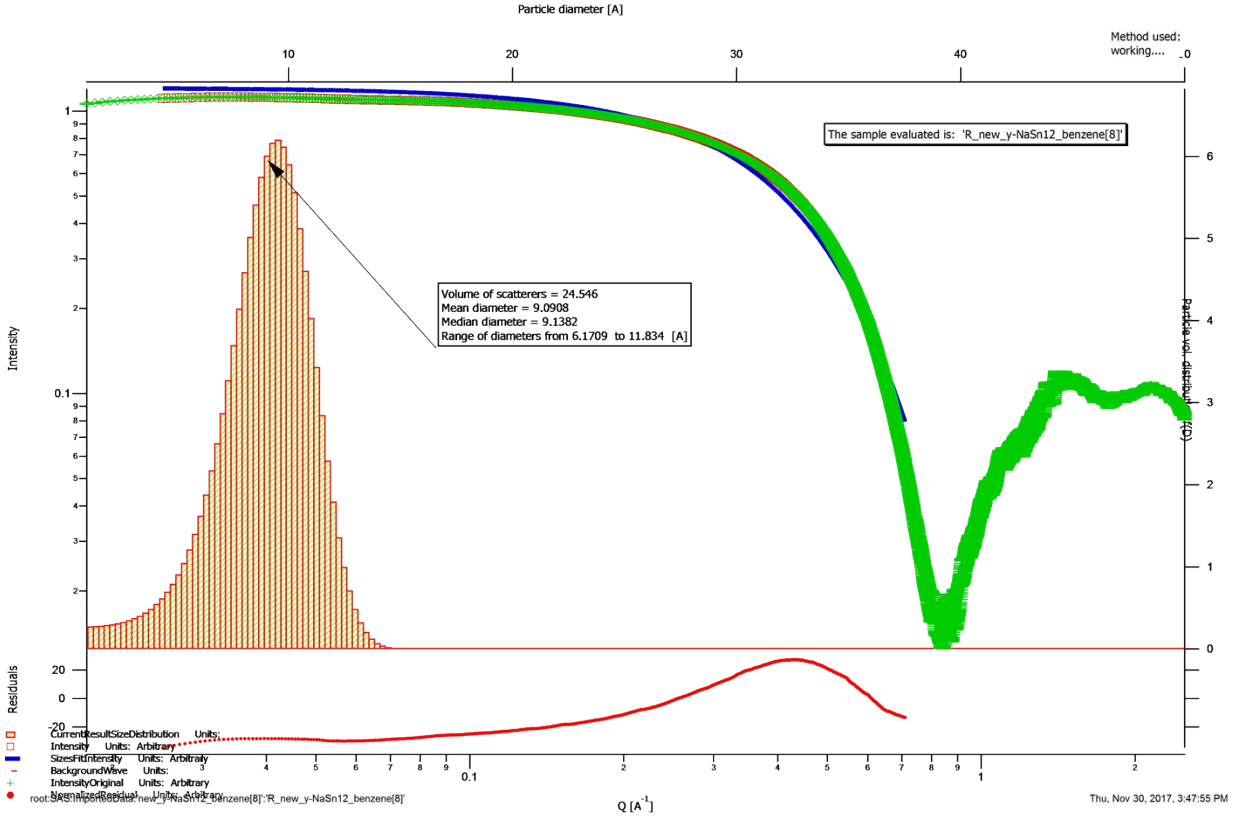

Figure SI10: Size distribution analysis of SAXS data of β,γ-$NaSn_{12}$ in benzene.

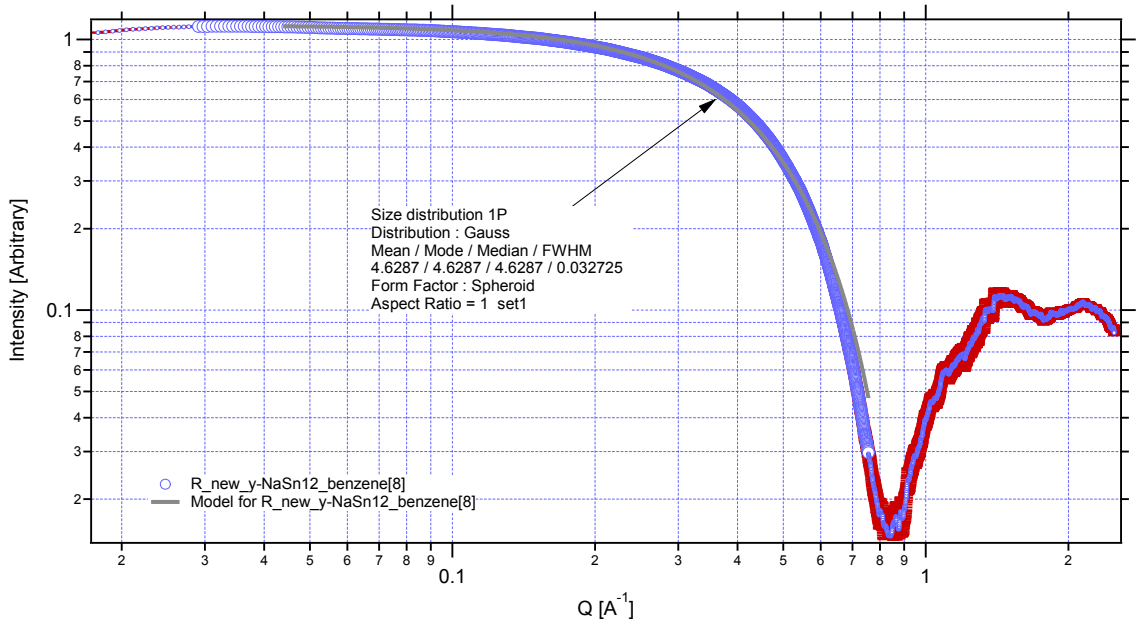

Figure SI11: Modelling II results for β,γ-$NaSn_{12}$ in benzene. The experimental scattering curve is in red and the calculated model in gray. The calculated radius is consistent with the radius determined from the experimental crystal structure.

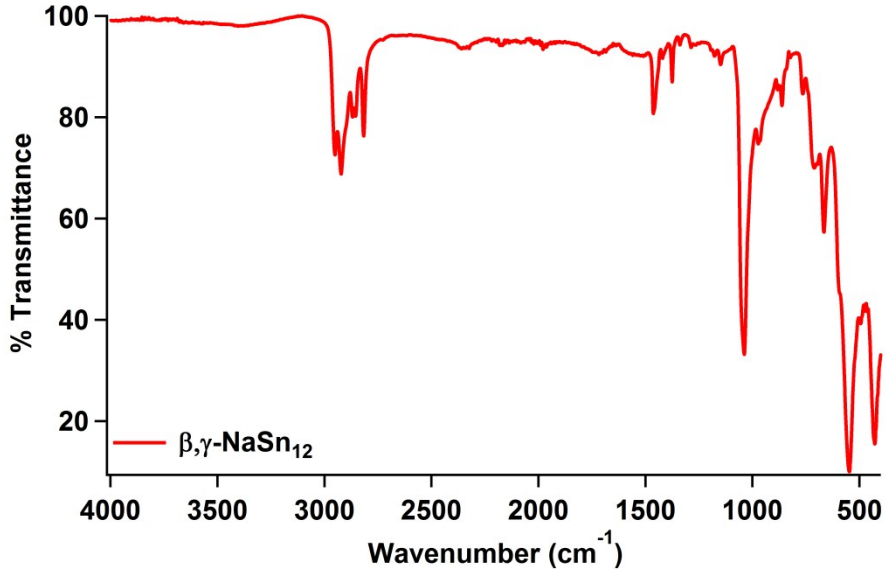

Figure SI12: IR spectrum of β,γ-$NaSn_{12}$ showing the presence of methoxy ligands indicated by the strong C-O stretch at 1038 cm^{-1}.

REFERENCES

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09*, Gaussian, Inc., Wallingford, CT, 2013.